

AD-A153 134

THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES(U)  
PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF  
CHEMISTRY H R ALLCOCK 29 JAN 85 ARO-18930.19-CH

1/1

UNCLASSIFIED

DAG29-82-K-0045

F/G 7/3

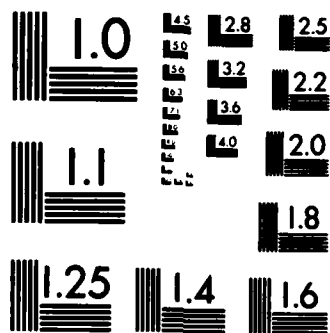
NL

END

FILMED

DTIC





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A153 134

DTIC FILE COPY

UNCLASSIFIED  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MASTER COPY - FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>ARO 18930.19-CH</b>	2. GOVT ACCESSION NO. <b>N/A</b>	3. RECIPIENT'S CATALOG NUMBER <b>N/A</b>
4. TITLE (and Subtitle) <b>The Synthesis and Structure of Polyphosphazenes</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Final 12/9/81 - 12/8/84</b>
		6. PERFORMING ORG. REPORT NUMBER
AUTHOR(s) <b>Harry R. Allcock</b>		8. CONTRACT OR GRANT NUMBER(s) <b>DAAG29-82-K-0045</b>
PERFORMING ORGANIZATION NAME AND ADDRESS <b>Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
CONTROLLING OFFICE NAME AND ADDRESS <b>U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709</b>		12. REPORT DATE <b>January 29, 1985</b>
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES <b>4</b>
		15. SECURITY CLASS. (of this report) <b>Unclassified</b>
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) <b>Approved for public release; distribution unlimited.</b>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) <b>NA</b>		
18. SUPPLEMENTARY NOTES <b>The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.</b>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <b>Polymers, polyphosphazenes, phosphazenes, metallo-polymers, polymer structure.</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>New polyphosphazenes have been designed and synthesized, and the structure of these materials has been investigated.</b>		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MAY 1 1985

ARO 18930.19-CH

THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES

FINAL REPORT

Harry R. Allcock

January 29, 1985

U.S. Army Research Office

Grant Number DAAG-2982-K-0045

Department of Chemistry  
The Pennsylvania State University  
University Park, Pennsylvania 16802

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



### Statement of the Problem Studied

Macromolecules (also known as polymers) are very large molecules that are integral components of structural plastics, elastomers, textile fibers, films, and coating materials--all of great importance to both the military and civilian sectors. With the exception of the silicones, virtually all polymers are "organic"-type substances derived either from petrochemicals or directly from living things.

A number of years ago, we discovered an entirely new class of polymers, called polyphosphazenes. These differ from conventional macromolecules because they have a backbone structure composed of inorganic elements in the form of alternating phosphorus and nitrogen atoms, and with two organic groups attached to each phosphorus atom.

These polymers have now been developed technologically in a number of different laboratories, including the Army Materials and Mechanics Laboratory at Watertown, Massachusetts, and by industrial companies.

During the grant period 1981 to 1984, we have sought to advance the knowledge of this field in three ways. First, we have explored the possibility that polyphosphazenes can be synthesized that will optimize film-forming properties. Such films could be of wide use in engineering applications, or as protective barrier materials in a hostile environment. Second, we have pioneered a new chemistry of polyphosphazenes that allows transition metals to be incorporated into the side groups attached to a polyphosphazene chain. Such new materials are of interest for their prospective electroactive properties and as polymer-bound catalysts, perhaps for use in batteries or fuel cells. Finally, we recognized that the design and synthesis of new polymers cannot be undertaken efficiently unless a thorough understanding is available of the reasons why specific molecular structural features give rise to certain properties, such as polymer strength, flexibility, or electrical conductivity. Thus, a critical part of our program has been to obtain molecular structural information for these new polymers and to correlate these data with the observed properties.

### Summary of the Most Important Results

→ Film-forming polyphosphazenes have been developed based on mixed substituent polymers, especially those with both hydrophilic and hydrophobic substituents. The surface hydrophobicity of such polymers has been studied as a function of the side group ratios.

→ A variety of different synthetic methods have been devised and developed for the linkage of metal-containing groups to a phosphazene skeleton. These include the reactions of lithioferrocene or lithioruthenocene with halogeno-phosphazenes, the reactions of organometallic anions, such as  $\text{NaFe}(\text{CO})_2\text{Cp}$ ,  $\text{Na}_2\text{Fe}_2(\text{CO})_8$ ,  $\text{Bu}_4\text{N}(\text{CO})_3\text{Cp}$ ,  $\text{Bu}_4\text{NMo}(\text{CO})_3\text{Cp}$ , and  $\text{Bu}_4\text{NW}(\text{CO})_3\text{Cp}$ . Similar derivatives have been prepared by the reactions of phosphazene anions with organometallic halides. These metallophosphazenes constitute a new class of compounds which, at the high polymeric level, should give rise to unusual electronic, catalytic, or thermal behavior.

Continued  
Finally, major progress has been made in understanding the relationship between molecular structure and physical properties of polyphosphazenes by the synthesis and X-ray diffraction study of a series of linear short chain analogues of the high polymers. The new structural data can now be applied to the high polymers to explore the reasons for unusual phenomena such as the low glass transition temperatures and the crystallization behavior.

List of Publications (grant # DAAG29-82-K-0045)

Phosphine-Linked Phosphazenes as Carrier Molecules for Transition Metal Complexes, H. R. Allcock, K. D. Lavin, N. M. Tollefson, and T. L. Evans, Organometallics 1983, 2, 267-275.

Iron- and Ruthenium-Linked Phosphazenes, H. R. Allcock, L. J. Wagner, and M. L. Levin, J. Am. Chem. Soc. 1983, 105, 1321-1327.

An Improved Method for the Synthesis of Poly(organophosphazenes) and Hindered Cyclophosphazenes, P. E. Austin, G. H. Riding, and H. R. Allcock, Macromolecules 1983, 16, 719-722

A New Approach to Polymer Chemistry: Organometallic and Bioactive Phosphazenes, H. R. Allcock, J. Polymer Sci., Polymer Symposia 1983, Vol 70, 71-77.

Iron-Bound Cyclotriphosphazene Derived from Phosphazene Anions. X-Ray Crystal Structure of  $N_3P_3Cl_4(CH_3)[Fe(CO)_2(C_5H_5)]$ , R. A. Nissan, M. S. Connolly, M. G. M. Mirabelli, R. R. Whittle, and H. R. Allcock, J. Chem. Soc., Chem. Commun. 1983, 822-824.

Cyclic and High Polymeric Phosphazenes as Carrier Molecules for Carboranyl, Metallo, or Bioactive Side Groups, Chapter in "Rings, Clusters, and Polymers of the Main Group Elements", ACS Symp. Ser. 1983, 232, 46-67.

Dicobalt-Hexacarbonyl Complexes of Acetylenic Phosphazenes, H. R. Allcock, R. A. Nissan, P. J. Harris, and R. R. Whittle, Organometallics 1984, 3, 432-440.

Synthesis and Structure of Metallocene Cyclophosphazene Derivatives, H. R. Allcock, K. D. Lavin, G. H. Riding, P. R. Suszko, and R. R. Whittle, J. Am. Chem. Soc. 1984, 106, 2337-2347.

The Reaction of Mono- and Dilithioferrocene with Octachlorotetra-phosphazene: The Crystal and Molecular Structures of  $N_4P_4Cl_6[(n-C_5H_4)Fe-(n-C_5H_5)]_2$  and  $N_3P_3Cl_4(n-C_5H_4)Fe(n-C_5H_5)N_4P_4Cl_7$ , Organometallics 1984, 3, 663-669.

Iron-Containing Metallophosphazenes and Their Clusters Derived from Chlorophosphazenes and Organometallic Dianions, H. R. Allcock, P. R. Suszko, L. J. Wagner, R. R. Whittle, and B. Boso, J. Am. Chem. Soc. 1984, 106, 4966-4977.

Chromium, Molybdenum, and Tungsten Chlorophosphazenes: Molecular Structures of  $N_3P_3Cl_5[Cr(CO)_3(\eta-C_5H_5)]$  and  $N_3P_3Cl_4(C_5H_5)[Mo(\eta-C_5H_5)]$ , H. R. Allcock, G. H. Riding, and R. R. Whittle, J. Am. Chem. Soc. **1984**, 106, 5561-5567.

Metal Exchange Reactions Under the Influence of a Cyclophosphazene Template: Iron, Cobalt, and Rhodium Metallophosphazenes, H. R. Allcock, P. R. Suszko, L. J. Wagner, R. R. Whittle, and B. Boso, Organometallics (in press).

Reactions Between Hexachlorocyclotriphosphazene and Hexamethylcyclotrisiloxane: Polymerization, Ring Cleavage, and Crosslinking, H. R. Allcock, D. J. Brennan, and R. W. Allen, Macromolecules (in press).

Ring-Opening Polymerization of Metallocene Cyclophosphazene Derivatives, H. R. Allcock, K. D. Lavin, and G. H. Riding, Macromolecules (in press).

Conformation, Bonding, and Flexibility in Short-Chain Linear Phosphazenes, H. R. Allcock, N. M. Tollefson, R. A. Arcus, and R. R. Whittle, J. Am. Chem. Soc. (submitted).

Progress Reports Sent to ARO (grant # DAAG29-82-K-0045)

Progress Report No. 26	(Period covered by report	7/1/82-12/31/82)
Progress Report No. 27	( " " " "	1/1/83-6/30/83)
Progress Report No. 28	( " " " "	7/1/83-12/31/83)
Progress Report No. 29	( " " " "	1/1/84-6/30/84)
Progress Report No. 30	( " " " "	7/1/84-12/31/84)

Personnel Supported by this Project and Degrees Awarded

H. R. Allcock	(Principal Investigator)	
G. H. Riding	(Postdoctoral Fellow)	
R. R. Whittle	(Crystallographer)	
P. R. Suszko	(Graduate Fellow)	Ph.D. awarded 1983
L. J. Wagner	(Graduate Fellow)	Ph.D. awarded 1984
N. M. Tollefson	(Graduate Fellow)	Ph.D. awarded 1983
D. J. Brennan	(Graduate Fellow)	
M. Mang	(Graduate Fellow)	
G. Schrubbe	(Graduate Fellow)	



**END**

**FILMED**

**5-85**

**DTIC**











